

HYDRATED SODIUM-COBALT OXIDE

TECHNICAL FIELD

5 The present invention relates to a hydrated sodium-cobalt oxide exhibiting superconductivity.

BACKGROUND ART

As a sodium-cobalt oxide comprising a CoO_2 layer wherein CoO_6 octahedra each having a
10 cobalt atom coordinated with six oxygen atoms are linked in an edge-sharing manner, α -type (rhombohedral system), α' -type (monoclinic system), β -type (orthorhombic system) and γ -type (hexagonal system) were found in 1973 (see Non-Patent Publication 1). This publication reports that these systems have a crystal structure formed of cobalt – oxygen – sodium – oxygen – cobalt layers laminated in this order, and a distance between the adjacent cobalt layers (cobalt
15 interlayer distance) of 5.19 Å, 5.38 Å, 5.51 Å and 5.44 Å, respectively.

It is also known that a change in cobalt interlayer distance is caused by deintercalation or intercalation of sodium ions from/to the above sodium-cobalt oxides. For example, sodium-cobalt oxides of Na_xCoO_2 ($x = 0.82, 0.90, 0.95$) obtained in this way have cobalt interlayer distances of 5.52 Å, 5.51 Å and 5.38 Å, respectively (see Non-Patent Publication 2),
20 and sodium-cobalt oxides of Na_xCoO_2 ($x = 0.5, 0.6$) have cobalt interlayer distances of 5.51 Å and 5.56 Å, respectively (see Non-Patent Publication 3). As above, the cobalt interlayer distance in the known layer-structured sodium-cobalt oxides is in the range of 5 Å to 6 Å.

Therefore, great interest has been industrially shown in the following characteristics of sodium-cobalt oxides: (1) extremely large thermoelectric power and (2) potential ability as a
25 precursor for synthesizing a lithium-cobalt oxide.

As to thermoelectric effect, since a large thermoelectromotive force was found in a NaCo_2O_4 single crystal in 1997 (see Non-Patent Publication 4), sodium-cobalt oxides have been regarded as one of noteworthy thermoelectric materials, and a previously reported material includes (Na, Ca) Co_2O_4 (see Non-Patent Publication 5) and $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ (see Non-Patent

Publication 6).

A lithium-cobalt oxide represented by LiCoO_2 is currently use as an active material for a positive electrode in lithium-ion secondary batteries. This oxide has the same CoO_2 layer as that of the aforementioned sodium-cobalt oxides. A sodium-cobalt oxide used as a precursor for substituting a sodium ion residing between CoO_2 layers with a lithium ion makes it possible to obtain a lithium-cobalt oxide having a layer structure laminated in a different manner as compared to that to be obtained through a conventional solid-phase reaction process (see Non-Patent Publication 7). It has been disclosed that such a lithium-cobalt oxide can also be used as a material for a positive electrode in lithium-ion secondary batteries (see Non-Patent Publication 8).

Non-Patent Publication 1: C. Fouassier, G. Matejka, J. -M. Reau, and P. Hagenmuller, J. Solid State Chem., 6, pp. 532-537 (1973)

Non-Patent Publication 2: J. -J. Braconnier, C. Delmas, C. Fouassier, and P. Hagenmuller, Mat. Res. Bull., 15, pp. 1797-1804 (1980)

Non-Patent Publication 3: S. Kikkawa, S. Miyazaki, and M. Koizumi, J. Solid State Chem., 62, pp. 35-39 (1986)

Non-Patent Publication 4: I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 56, pp. R12685-R12687

Non-Patent Publication 5: Y. Ando, N. Miyamoto, K. Segawa, and I. Terasaki, Phys. Rev. B 60, pp. 10580-10583 (1999)

Non-Patent Publication 6: I. Terasaki, Y. Ishii, D. Tanaka, K. Takahashi, and Y. Iguchi, Jpn. J. Appl. Phys. 40, pp. L65-L67 (2001)

Non-Patent Publication 7: C. Delmas, J. -J. Braconnier, and P. Hagenmuller, Mat. Res. Bull., 17, pp. 117-123 (1982)

Non-Patent Publication 8: J. M. Paulsen, J. R. Muller-Neuhaus, and J. R. Dahn, J. Electrochem. Soc., 147, pp. 508-516 (2000)

DISCLOSURE OF INVENTION

In view of the above circumstance, it is an object of the present invention to provide a

sodium-cobalt oxide having a cobalt interlayer distance of 9.5 Å to 10.5 Å which is significantly different from that of the known compounds, and exhibiting superconductivity at low temperature based on characteristics induced by the cobalt interlayer distance.

5 In order to achieve the object, the present invention provides a hydrated sodium-cobalt oxide comprising a plurality of CoO_2 layers each having edge-sharing CoO_6 octahedra, and a combination of two water molecule layers and a single sodium ion layer, which is interposed between the adjacent CoO_2 layers.

Preferably, the distance between the adjacent CoO_2 layers is in the range of 9.5 to 10.5 Å.

10 The present invention also provides a hydrated sodium-cobalt oxide, which is represented by the following general formula: $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$, wherein $0 < x \leq 0.4$, and $1.0 \leq y \leq 2.0$.

Furthermore, the present invention also provides a method of producing a hydrated sodium-cobalt oxide, comprising; synthesizing, from a sodium compound and a cobalt compound, Na_xCoO_2 which comprises a plurality of CoO_2 layers each having edge-sharing CoO_6 octahedra, and a single sodium ion layer interposed between the adjacent CoO_2 layers; 15 deintercalating a part of the sodium ions from said Na_xCoO_2 ; and then intercalating a water molecule between the adjacent CoO_2 layers.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic diagram showing a crystal structure model of a parent compound 20 $\text{Na}_{0.7}\text{CoO}_2$ and a hydrated sodium-cobalt oxide, in Inventive Example 1.

FIG. 2 is a graph showing a powder X-ray diffraction pattern and a Rietveld analysis result of the hydrated sodium-cobalt oxide in Inventive Example 1.

FIG. 3 is a graph showing a measurement result about electrical resistance of the hydrated sodium-cobalt oxide in Inventive Example 1.

25 FIG. 4 is a graph showing a measurement result about magnetic susceptibility of the hydrated sodium-cobalt oxide in Inventive Example 1.

FIG. 5 is a graph showing a powder X-ray diffraction pattern and a Rietveld analysis result of a product obtained in Comparative Example 1.

FIG. 6 is a graph showing a measurement result about magnetic susceptibility of the

product obtained in Comparative Example 1 (●) and the hydrated sodium-cobalt oxide obtained in Inventive Example 1 (○).

FIG. 7 is a graph showing a powder X-ray diffraction pattern of a product obtained in Comparative Example 2.

FIG. 8 is a graph showing a measurement result about magnetic susceptibility of the product obtained in Comparative Example 2 (●) and the hydrated sodium-cobalt oxide obtained in Inventive Example 1 (○).

BEST MODE FOR CARRYING OUT THE INVENTION

A hydrated sodium-cobalt oxide of the present invention is obtained by deintercalating, from a parent compound Na_xCoO_2 , a part of the sodium ions residing between CoO_2 layers, and then intercalating water molecules between the CoO_2 layers.

For example, even if the parent compound Na_xCoO_2 is simply immersed in water, it is difficult to intercalate water molecules between the layers. The partial deintercalation of the interlayer sodium ions makes it possible to achieve this intercalation. Supposedly, the reason is that, as the result as the partial deintercalation of the sodium ions, a number of vacant sites capable of intercalating water molecules therein are formed around the remaining sodium ions, and the charge between the CoO_2 layers gets close to neutral so as to reduce an electrostatic interaction (electrostatic attraction force) between CoO_2 layer-Na layer- CoO_2 layer to facilitate increase in interlayer distance, whereby water molecules are intercalated, and the distance between the CoO_2 layers is increased.

The hydrated sodium-cobalt oxide obtained in this way has a previously unknown structure in which a single sodium ion layer and two water molecule layers are interposed between the CoO_2 layers as shown in FIG. 1, and the cobalt interlayer distance is increased up to about 9.8 Å.

In this hydrated sodium-cobalt oxide, the distance between the CoO_2 layers is largely increased, and the CoO_2 layers are laminated while interposing a combination of the sodium ion layer and the water molecule layers therebetween, which leads to a significant low interlayer interaction. Thus, conduction electrons are confined within an extremely limited 2-dimensional space of each CoO_2 layer, and thereby the inter-electron interaction in the CoO_2 layer becomes

significantly stronger to provide superconductivity.

The parent compound Na_xCoO_2 may be synthesized by a convention process comprising mixing a sodium source and a cobalt source, and heating the mixture in an oxygen-containing atmosphere. This conventional process may include a process using sodium peroxide (Na_2O_2) and cobalt oxide (Co_3O_4) (Process 1: see the aforementioned Non-Patent Publication 1), a process using sodium oxide (Na_2O) and cobalt oxide (Co_3O_4) (see "A. Stoklosa, J. Molenda, and D. Than, Solid State Ionics, 15, pp. 211-216 (1985)), and a process using sodium carbonate (Na_2CO_3) and cobalt carbonate (CoCO_3) (Process 2: R. J. Balsys and R. L. Davis, Solid State Ionics, 93, pp. 279-282 (1996)). These processes may be used independently or in combination as a process for synthesizing the Na_xCoO_2 .

In the parent compound Na_xCoO_2 , a preferable range (x) of the sodium composition is $0.5 \leq x \leq 1.0$. If the sodium composition is less than the lower limit of this range, the cobalt oxide is liable to remain. If the sodium composition is greater than the upper limit of this range, Na_4CoO_4 is liable to be mixed as an impurity.

While the Na_xCoO_2 obtained in the way exhibits various crystal structures disclosed, for example, in the aforementioned Non-Patent Publication 1, its crystal structure fundamentally comprises CoO_2 layers each having edge-sharing CoO_6 octahedra, and a single sodium ion layer interposed between the CoO_2 layers, wherein a cobalt interlayer distance is in the range of 5 Å to 6 Å.

The deintercalation of sodium ions from the parent compound may be performed through a conventional process, for example, a chemical process using an oxidizing reagent, such as iodine or bromine (S. Miyazaki, S. Kikkawa, and M. Koizumi, Synthetic Met. 6, pp. 211-217 (1983)), or a process based on electrochemical oxidation (J. J. Braconnier, C. Delmas, C. Fouassier, and P. Hagenmuller, Mat. Bull., 15, pp. 1797-1804 (1980)).

The intercalation of water molecules may be performed in the most simplified manner through a process comprising immersing in water the above compound whose sodium ions have been partly deintercalated. Alternatively, it may be a process comprising exposing the compound to a humid atmosphere.

A hydrated sodium-cobalt oxide to be obtained through the above method comprises a

plurality of CoO_2 layers each having approximately the edge-sharing CoO_6 octahedra as those of the parent compound, and a combination of two water molecule layers and a single sodium ion layer, which is interposed between the adjacent CoO_2 layers, wherein the distance between the adjacent CoO_2 layers is in the range of 9.5 to 10.5 Å.

5 The number of water molecules intercalated between the CoO_2 layers is varied depending on humidity. Specifically, the intercalation of water molecules is induced by exposing the hydrated sodium-cobalt oxide to a high-humidity atmosphere. By contrast, the deintercalation is induced by exposing the hydrated sodium-cobalt oxide to a low-humidity atmosphere. Each of Co atoms has two sites to be occupied by water molecules (in the after-mentioned structural
10 analysis, water molecules are allocated to six sites residing in each Co atom illustrated in FIG. 1 because water molecules actually diffuse between the CoO_2 layers). Thus, the number of water molecules to be intercalated between the CoO_2 layers is two at a maximum. Further, if the number of interlayer water molecules is reduced, the molecules cannot form a two-layer structure, and will simply occupy vacant sites in the sodium layers. Therefore, in the hydrated
15 sodium-cobalt oxide of the present invention, the number of water molecules is between one and per Co atom. That is, in a general formula: $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ representing the hydrated sodium-cobalt oxide, this relation is expressed by $0 < x \leq 0.4$, and $1.0 \leq y \leq 2.0$.

(EXAMPLE)

20 The present invention will be described in detail in connection with the following examples.

(Inventive Example 1)

In this example, a sodium-cobalt oxide expressed by $\text{Na}_{0.7}\text{CoO}_2$ was synthesized. After deintercalating a part of sodium ions using bromine, water molecules were intercalated between CoO_2 layers to prepare a hydrated sodium-cobalt oxide expressed by $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$.

25 In the synthesis of the $\text{Na}_{0.7}\text{CoO}_2$, sodium carbonate (Na_2CO_3) and cobalt oxide (Co_3O_4) were used as a starting material. These starting materials were weighted and mixed together to satisfy the relationship: $[\text{Na}]/[\text{Co}] = 0.7/1.0$, and the obtained mixture was pelletized through an uniaxial pressing process. The obtained pellets were heated at 800°C in an oxygen flow for 8 hours to obtain the $\text{Na}_{0.7}\text{CoO}_2$. According to the analysis by powder X-ray diffractometry, it

was verified that the obtained compound has the same crystal structure as that disclosed in the aforementioned Process 2. Specifically, the compound had a lattice constant $a = 2.8281 (3) \text{ \AA}$ and $c = 10.9658 (11) \text{ \AA}$. That is, a cobalt interlayer distance was about 5.48 \AA .

5 The deintercalation of sodium ions from the obtained $\text{Na}_{0.7}\text{CoO}_2$, and the intercalation of water molecules therein were performed through the following process. The synthesized $\text{Na}_{0.7}\text{CoO}_2$ was firstly crushed and weighted. With respect to the amount of sodium in the weighted $\text{Na}_{0.7}\text{CoO}_2$ powder, 5 parts of bromine was dissolved in acetonitrile to prepare an acetonitrile solution of bromine. Then, the $\text{Na}_{0.7}\text{CoO}_2$ powder was immersed in this solution, and left at room temperature for 5 days to deintercalate a part of sodium ions from between the
10 $\text{Na}_{0.7}\text{CoO}_2$ layer. The obtained power was filtered and cleaned to remove unreacted bromine using acetonitrile, and then immersed in distilled water to intercalate water molecules between the CoO_2 layers.

For determining the composition of the hydrated sodium-cobalt oxide obtained in this way, the respective contents of sodium and cobalt were measured by inductively-coupled plasma
15 atomic emission spectrometry (ICP-AES). As a result, it was proven that this oxide has a composition of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$.

Based on the result of the powder X-ray diffractometry, the structure of this hydrated sodium-cobalt oxide was refined through a Rietveld refinement method using the same space group ($\text{P6}_3/\text{mmc}$) as that of the structure of the parent compound $\text{Na}_{0.7}\text{CoO}_2$. The result of the
20 Rietveld analysis is shown in Table 1. A refined lattice constant was $a = 2.8230 (2) \text{ \AA}$ and $c = 19.6207 (14) \text{ \AA}$, and structural parameters were as shown in Table 1. In Table 1, the refinement was performed on the assumption that the interlayer water molecules is WO having a scattering factor equal to the total of the scattering factors of one oxygen atom and two hydrogen atoms. Further, U indicates an isotopic atom displacement parameter, and the content of sodium was
25 fixed at the result of the ICP-AES.

Table 1

Atom	Site	Fractional Coordinate			Occupancy	U/ Å
		x	y	z		
Co	2a	0	0	0	1	0.0063 (6)
O	4f	1/3	2/3	0.0451 (3)	1	0.0162 (12)
Na1	2d	2/3	1/3	1/4	0.159 (4)	= U (O)
Na2	2b	0	0	1/4	0.192	= U (O)
WO1	12k	0.174 (13)	= 2x (WO1)	0.1793 (2)	0.070 (12)	= U (O)
WO2	12k	0.370 (12)	= x (WO2)/2	= z (WO1)	0.176 (12)	= U (O)

FIG. 2 shows a powder X-ray diffraction pattern and a Rietveld analysis result of the hydrated sodium-cobalt oxide in Inventive Example 1. In FIG. 2, the mark +: measurement value, the solid line: calculation value, the vertical bar: Bragg reflection position, and the lower solid line: the difference between the measurement and calculation values. The obtained R factors had low values, specifically, $R_B = 2.84\%$ and $R_F = 3.53\%$. Further, as shown in FIG. 2, the calculated diffraction pattern based on the structural model well corresponds to the actual measurement value. This proves that this structural model is adequate as the crystal structure of the hydrated sodium-cobalt oxide obtained in Inventive Example 1.

As evidenced by the above results, as shown in FIG. 1, the obtained hydrated sodium-cobalt oxide comprises approximately the same CoO_2 layers as those of the parent structure, and a combination of a single sodium ion layer and two water molecule layers, which is intercalated between the CoO_2 layers, and has a cobalt interlayer distance of 9.81 \AA , which is extremely long as compared with the parent structure.

The superconductivity of the obtained hydrated sodium-cobalt oxide was checked by resistivity measurement using a four-terminal method, and magnetic-susceptibility measurement using a SQUID (Superconducting Quantum Interference Device). FIG. 3 shows the result of the resistivity measurement in a zero magnetic field. The hydrated sodium-cobalt oxide exhibited a sharp change of resistivity at about 5 K and fell off.

The magnetic-susceptibility measurement was performed under the conditions of a zero-field cooling in a temperature range of 2 K to room temperature, wherein a measurement magnetic field was set at 20 Oe. The result is shown in FIG. 4. This measurement value at 2K is equivalent to 13 % of a theoretical value ($-1/4 \pi \text{ emu/cm}^3$) in perfect diamagnetism.

Considering this result together with that of resistivity measurement, it was verified that this material exhibits superconductivity.

(Comparative Example 1)

In this example, a hydrated sodium-cobalt oxide having no intercalated water molecule was synthesized, and its superconductivity characteristic was checked. The synthesis of the parent compound $\text{Na}_{0.7}\text{CoO}_2$ and the partial deintercalation of sodium ions were performed in the same manner as those in Inventive Example 1. Acetonitrile used as a solvent of bromine and for removing excessive bromine was removed by vaporization under reduced pressure.

FIG. 5 shows a powder X-ray diffraction pattern of a compound obtained in this way. In FIG. 5, the mark +: measurement value, the solid line: calculation value, the vertical bar (upper): Bragg reflection position corresponding to sodium bromide, the vertical bar (lower): Bragg reflection position corresponding to sodium-cobalt oxide, and the lower solid line: the difference between the measurement and calculation values. As a result, it was proven that the obtained material is a mixture of a sodium-cobalt oxide having approximately the same crystal structure (space group: $\text{P6}_3/\text{mmc}$, $a = 2.8184(4) \text{ \AA}$, $c = 11.1532(13) \text{ \AA}$) as that of the parent compound, and sodium bromide.

FIG. 6 shows a measurement result about magnetic susceptibility of this mixture using a SQUID, wherein the vertical axis represents magnetic susceptibility per Co atom residing in the mixture. In this mixture, no decrease in magnetic susceptibility was observed in a temperature of 2 K or more, and no superconducting phase was created.

(Comparative Example 2)

In this example, a part of water molecules in the hydrated sodium-cobalt oxide obtained in Inventive Example 1 was deintercalated to synthesize a sodium-cobalt oxide having a single water molecule layers, and its superconductive characteristic was checked. The partial deintercalation of water molecules was performed by exposing the hydrated sodium-cobalt oxide obtained in Inventive Example 1, to a nitrogen flow for one week.

A powder X-ray diffraction pattern of the obtained material is shown in FIG. 7. The resulting diffraction peak can be indexed using the unit cell of a hexagonal system as with the hydrated sodium-cobalt oxide obtained in Inventive Example 1. A lattice constant calculated

based on this unit lattice was $a = 2.8301(12) \text{ \AA}$, and $c = 13.834(6) \text{ \AA}$.

That is, the distance between the CoO_2 layers is about 7 \AA . Thus, this structure would have only one water molecule layer between the CoO_2 layers.

A measurement result about magnetic susceptibility of this mixture using a SQUID is shown in FIG. 8. In this mixture, while some decrease in magnetic susceptibility was observed from around 5 K , the magnetic susceptibility did not have a negative value even if the temperature was reduced to 2 K . The decrease in magnetic susceptibility corresponds to the characteristic at a transition temperature to a superconducting phase in the hydrated sodium-cobalt oxide obtained in Inventive Example 1. Thus, it is believed that this decrease is induced by the remaining portion of the hydrated sodium-cobalt oxide obtained in Inventive Example 1.

In this connection, no existence of the remaining phase was observed by the powder X-ray diffractometry, because this remaining amount was an extremely small value according to the calculation based on the decrease in magnetic susceptibility ($1 \times 10^{-3} \text{ emu/mol}$) observed in Comparative Example 2, and the decrease in magnetic susceptibility ($4 \times 10^{-3} \text{ emu/mol}$) observed in Inventive Example 1.

INDUSTRIAL APPLICABILITY

The hydrated sodium-cobalt oxide of the present invention has an extremely wide interlayer distance increased to about 9.8 \AA , and includes highly diffusible sodium ions and water molecules between the layers. Thus, based on high ability of ion-exchanging with various ion species and molecules, the hydrated sodium-cobalt oxide can be effectively used as a precursor for synthesizing compounds through ion exchanging. In addition, this hydrated sodium-cobalt oxide is the first cobalt oxide exhibiting superconductivity. Thus, the synthesis of various compounds using this material as a precursor is significant valuable in researches on new superconducting materials.